REPLY TO THE COMMENT BY VIDAL, DUBACQ, AND LANARI ON "THE ROLE OF H_3O^+ IN THE CRYSTAL STRUCTURE OF ILLITE"

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Abstract—The arguments of Vidal *et al.* (2010) against the incorporation of H_3O^+ rather than of H_2O in the interlayer position of illite are disputable. Stoichiometric arguments do indeed suggest that the excess water in the Silver Hill illite is in the form of H_3O^+. No reason exists to assume less water content in the IMt-2 sample than in those determined by Hower and Mowatt (1966) and confirmed by the thermogravimetric analyses of Nieto *et al.* (2010). The comparison between element contents calculated from end-members and those from the structural formula in figure 1 of Vidal *et al.* (2010) is not an experimental result, but rather a trivial mathematical artifact. The fact that thermodynamic models, based on the incorporation of interlayer H_2O in illite, may provide reasonable estimates neither proves nor disproves the presence of H_3O^+; this is because thermodynamics is a non-atomistic, macroscopic approach.

Key Words—Composition, Hydronium, Illite, Water.

INTRODUCTION

Following the paper by Nieto *et al.* (2010), supporting the presence of hydronium ions, H_3O^+, in the crystal structure of illite, Vidal *et al.* (2010) argued that the excess water had to be in the form of H_2O rather than H_3O^+. Still convinced of the validity of the previous conclusions, the main points that justified the original interpretation of the data are re-presented here with respect to the comments made by Vidal *et al.* (2010).

THE ARGUMENTS

The H content of IMt-2 illite

One of the basic items of data for the conclusion by Nieto *et al.* (2010) about the nature of water in the illite structure was the thermogravimetric (TG) analysis. Correctly, Vidal *et al.* (2010) argue that TG cannot differentiate between H_2O and H_3O^+; TG does, however, give an accurate measure of the water content, which is essential for the assessment of the H content in the sample and the consequent adjustment of the structural formula. However, Vidal *et al.* (2010) begin their argument by questioning the water content, as taken from the original value suggested by Hower and Mowatt (1966). Vidal *et al.* attribute all the excess over 100% of the total in the analysis by Hower and Mowatt (1966) to errors in the water content (which is not a logical assumption) and consequently use a reduced water

content to justify the use of a reduced H content in their calculation of the formula of illite.

Taking into account the importance of an accurate measure of the water content, Nieto *et al.* (2010) carried out careful TG analysis, coupled with quadrupole mass spectrometry to detect the volatiles released. The aims of such an analysis were: (1) to check the original data by Hower and Mowatt (1966); (2) to ascertain that the weight loss corresponds almost exclusively to water; and (3) to distribute the overall water release among different structural positions, taking into account the different release temperature.

For point 1, agreement between the original data of Hower and Mowatt (1966), 6.4%, and those determined by Nieto *et al.* (2010), 6.86 wt.%, was good. Therefore, there is no reason to use an artificially reduced water content of 5.88% (as proposed by Vidal *et al.*, 2010) to calculate the H content. For point 2, the quadrupole mass spectrometer detected 18 and 17 as the most important mass/charge ratios, with smaller signals (approximately two orders of magnitude lower) at 44. Therefore, the weight loss was interpreted to be largely due to water-related species. Finally, for point 3, the TG curve showed two maximal emissions at 263°C and 556−658°C, corresponding to ~1.5 and 5.4 wt.%, respectively. The first peak was interpreted as being due to water loss from the interlayer, giving 0.85 H atoms per formula unit (a.p.f.u.), and the second peak, to layer dehydroxylation (2.00 H a.p.f.u.).

Provided that its measurement is sufficiently accurate, the H content can be used in the calculation of a formula with the same confidence as the other chemical elements. Such accuracy depends on (1) the quality of the analytical data and (2) the purity of the sample

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analyzed. For point 1, the similarity of the data of Hower and Mowatt (1966) and those of Nieto *et al.* (2010), obtained by different techniques, argues strongly in favor of the data quality. In addition, analysis by quadrupole mass spectrometry guarantees that the loss determined by the two methods is due to water. For point 2, the only significant contamination detected in sample IMt-2 by X-ray diffraction, transmission electron microscopy, and in previous research was from quartz. An admixed anhydrous phase would, in any case, produce a water content in the overall sample which is less than the actual water content of pure illite. The Hower and Mowatt (1966) and Nieto *et al.* (2010) water data represent a minimum value for pure illite. The real value cannot be less, however, as is assumed by Vidal *et al.* (2010).

In conclusion, the H content present in the interlayer of IMt-2 illite is, at least, 0.85 atoms (or molecules) per formula unit (a.p.f.u.), and this might represent 0.43 a.p.f.u. of neutral water (too many with respect to the vacant sites) or 0.28 of H_3O^+ (matching nicely the amount of vacant sites).

ORIGINAL DATA AND POSSIBLE ARTIFACTS

A second argument presented by Vidal *et al.* (2010) in favor of the speciation of the H present as neutral water in the interlayer of IMt-2 illite is based on the comparison between element contents calculated from the proportions of end-members and those from the structural formula (their figure 1). When they consider all the end-members assumed for the normalization of the formula to calculate the Si proportion, the result is a straight line (filled symbols in their figure 1). This is not an experimental result; it is, rather, a trivial mathematical fact (or circular argument), as the end-members are first calculated from the formula and, afterward, the elements again from the end-members, using in both cases the same theoretical assumptions.

The reason why this relationship does not exist in the case of incorporation of H_3O^+ (open symbols) is that XPrl, XPrlH, and XBt are implicitly assumed in the normalization of the formula based on 22 negative charges, but not for the calculation of Si content from the end-members. In addition, the formulae presented by Vidal *et al.* (2010) in their 'Case 2: interlayer vacancies filled by H_3O^{+}' are clearly different from those originally published in table 1 of Nieto *et al.* (2010) even though Vidal *et al.* (2010) refer to such data in the title of their table 1 ("...calculated from the AEM/TEM analyses of Nieto *et al.*, 2010"). We ignore the reason for such a difference, as the direct results of an AEM/TEM analysis are atomic proportions (as neatly formulated by Cliff and Lorimer, 1975) and the Nieto *et al.* (2010) data in their table 1 are normalized to 22 negative charges. Any other kind of computation, *e.g.* previous oxide percent calculation and recalculation of the

formula, lacks any physical meaning and produces only fictitious mathematical artifacts.

Hydronium-bearing minerals and pH conditions

The possible presence of the hydronium ion in illite had previously been suggested by Brown and Norrish (1952). It was further supported by White and Burns (1963) on the basis of the d_{001} value and a unique infrared absorption band at ~3470 cm^{-1}. Many other hydronium-bearing minerals are known, such as the zeolite fluoroapophyllite (Ishida and Kimata, 2007), hydronium-jarosite (*e.g.* Frost *et al.*, 2006), or H_3O^+-exchanged pharmacosiderite (Mills *et al.*, 2010). These minerals form under quite a range of conditions, not characterized by unrealistically low pH-values.

For illite, even allowing for pH conditions close to 4, the pH would not be very different from that occurring in many soils all over the world, often characterized by the presence of illite.

Furthermore, while considering the pH conditions, some consideration should also be given to the intrinsic basicity of the mineral. If the illite structure favors the presence of hydronium (as we believe), that mineral might behave like a buffer capable of fixing the hydronium produced by reactions occurring in sedimentary environments, such as that occurring in a soil solution or in a soil-water suspension. Here, Al and Fe occur as amphoteric hydroxides that react with water to release H_3O^+ (Stumm and Morgan, 1996), according to the equation:

$$Al(H_2O)_6^{3+} + H_2O = Al(H_2O)_5OH^{2+} + H_3O^+$$

Estimated temperatures

The final argument by Vidal *et al.* (2010) in favor of the neutral-water character of the H present in the interlayer of the IMt-2 sample is based on the use of the thermobarometric model of Dubacq *et al.* (2010) to calculate the temperature of formation of the IMt-2 sample using the data from Nieto *et al.* (2010). Unfortunately, as the real temperature of formation of sample IMt-2 is unknown, this argument also suffers from circular reasoning. In such conditions, the results presented in figure 2 of Vidal *et al.* (2010) may be considered to be "reasonable estimates of equilibrium conditions" as the authors claim, but can hardly be said to demonstrate the structural nature of the H present in the interlayer of the sample. A range of temperatures from 160 to 260ºC (for the majority of the analyses) could be considered to be "reasonable" or not for an immature illite consisting of a highly defective structure, a significant amount of 1M polytype, and a domain size for the illite packets of <10 layers.

Nieto *et al.* (2010) did not question the validity of the thermodynamic models previously published by Vidal and co-workers nor, in particular, by Dubacq *et al.* (2010). This group of geothermobarometric approaches

can be considered to be unique and innovative in the determination of thermodynamic conditions in low-temperature pelites. The fact that thermodynamic models may provide reasonable estimates, based on incorporation of interlayer H_2O in illite, neither proves nor disproves the presence of H_3O^+; because thermodynamics derives its predictive strength from its macroscopic nature, namely from the fact that thermodynamic formulations do not depend on the assumed state of matter. However, consideration of the possible nature of the water in the illite structure as H_3O^+ might constitute an adequate complement for the models.

CONCLUSION

In agreement with Dubacq *et al.* (2010) and Vidal *et al.* (2010), the presence of some kind of water species filling the interlayer spaces of illite to complete occupancy near to 1 a.p.f.u. is necessary. We are still convinced of the validity of the interpretation presented by Nieto *et al.* (2010) in terms of the presence of H_3O^+.

We also appreciate the stimulating debate, convinced that more research is needed to clarify this fundamental point. In particular, we look forward to further, direct determinations capable of producing better arguments in favor (as we feel) or against (as we do not!) the incorporation of H_3O^+ rather than H_2O in the interlayer position of illite.

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